

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
28 October 2004 (28.10.2004)

PCT

(10) International Publication Number
WO 2004/092240 A1

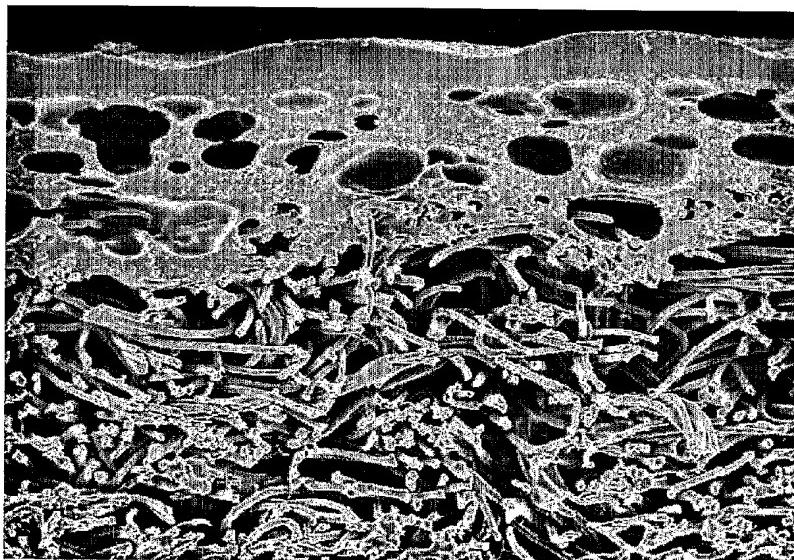
- (51) International Patent Classification⁷: **C08G 18/00**, D06N 3/14
- (74) Agent: **SOHN, Chang Kyu**; 4F., Halla Bldg., 641-17, Yoksam-dong, Kangnam-gu, Seoul 135-080 (KR).
- (21) International Application Number: PCT/KR2004/000879
- (22) International Filing Date: 16 April 2004 (16.04.2004)
- (25) Filing Language: Korean
- (26) Publication Language: English
- (30) Priority Data:
10-2003-0023966 16 April 2003 (16.04.2003) KR
10-2003-0023958 16 April 2003 (16.04.2003) KR
- (71) Applicant (for all designated States except US): **GETTROL [KR/KR]**; Namdong Industrial Park 131-12, 694-11, Kozan-dong, Namdong-gu, Inchon 405-310 (KR).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **KIM, Hyoung Soon [KR/KR]**; 202-202, Samik Apt., 166, Songpa 2-dong, Songpa-gu, Seoul 138-777 (KR). **CHOI, Kab Jin [KR/KR]**; Na-503, 355-9, Munhak-dong, Nam-gu, Incheon 402-070 (KR).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

[Continued on next page]

- (54) Title: WATER-BASED POLYURETHANE COMPOSITES AND SYNTHETIC LEATHERS OF NOVEL STRUCTURE



WO 2004/092240 A1

(57) Abstract: The present invention provides a water-based polyurethane composite useful in preparing a synthetic leather comprising fine particles having a mean diameter of 0.5 - 50 µm contained in a water-based polyurethane chain-extended product at 0.1 - 30% by weight on the basis of the total weight and also being in the viscosity range of 500 - 100,000 cps; and a water-based polyurethane synthetic leather of a novel structure in which an adhesive layer is added between a porous layer and a base layer to increase the adhesive strength between the porous layer and the base layer, thus the resulting synthetic leather can exhibit good properties such as a high adhesive strength, high chemical resistance, etc. and an excellent cushiony property, which is particularly useful as a material for shoes.



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WATER-BASED POLYURETHANE COMPOSITES AND SYNTHETIC LEATHERS OF NOVEL STRUCTURE

FIELD OF THE INVENTION

5 The present invention relates to a water-based polyurethane composite and a water-based polyurethane synthetic leather of a novel structure, and more specifically, (a) a water-based polyurethane composite useful in preparing a synthetic leather, which comprises fine particles having a mean particle diameter of 0.5 ~ 50 μm contained in a water-based polyurethane chain-extended product at 0.1 ~ 30% by weight on the basis of the total weight and also which is in the viscosity range of 500 ~ 100,000 cps; and (b) a water-based polyurethane synthetic leather of a novel structure in which an adhesive layer is added between a porous layer and a base layer to increase the adhesive strength between the porous layer and the base layer, whereas an adhesive layer is added between a porous layer and a top skin layer in a conventional synthetic leather, such that the synthetic leather can exhibit good properties such as a high adhesive strength, high chemical resistance, etc. and an excellent cushiony property.

BACKGROUND OF THE INVENTION

Polyurethane resins have been applied to many fields due to various properties thereof, including synthetic leathers and coatings. Conventional processes for preparation of a synthetic leather using polyurethane resin are based upon, for example, a solvent system wherein an organic solvent such as dimethylformamide

(“DMF”) is added to a material for preparation of a porous layer and the resultant mixture is coated on a base fiber, which is then submerged in water to be cured, while the organic solvent being replaced with water, followed by removal of water to produce a porous structure. This is sometimes referred to as “wetting process” due to
5 the water submersion step. The most serious problem of this organic solvent system process is the use of an organic solvent causing air pollution. In recent, new regulations have been introduced to restrict materials and processes causing pollution. Therefore, in order to solve these problems, many trials have been conducted to prepare a synthetic leather using a water-based polyurethane resin.

10 The feature of water-based polyurethane process is essentially not to use organic solvents. In other words, in preparation of a polyurethane prepolymer, a hydrophilic component is added or incorporated to make a hydrophilic prepolymer and, while the prepolymer is dispersed in water, polymerization reaction is performed using a chain extender. As a result, a water-based polyurethane process does not use
15 organic solvents such as DMF, thereby not causing environmental pollution.

 This merit of water-based polyurethane process was successfully applied to a coating field, but not to a synthetic leather field. In order for synthetic leather to replace natural leathers, it must have a so-called cushiony (cushion-like) property, i.e., soft and resilient property; however, no conventional water-based polyurethane
20 synthetic leathers satisfy this requirement. That is because, in the conventional preparation process of manufacturing synthetic leather using water-based polyurethane, pores disappear and the structure becomes densified, thereby the cushiony property is not obtained. Extensive efforts have been made to solve this problem but no substantial results have not achieved. For example, an alternative has

been developed whereby thermally decomposable, inorganic materials are added to water-based polyurethane resin and decomposed by heating to produce gases, resulting in a porous structure; however, the porous structure thus prepared is weak and also the process is complicated. Meanwhile, many relevant companies have 5 facilities for manufacture of solvent-based polyurethane synthetic leathers. If these facilities could be employed themselves in a new process, it would be very desirable in view of manufacturing cost.

In FIG. 1, there is illustrated a configuration of the prior art synthetic leather 100 which comprises a base layer 200 of fabric or resin-impregnated fabric, a porous 10 layer 300 providing a cushiony property situated on the base layer 200, an adhesive layer 400 situated on the porous layer 300, and a top skin layer 500 situated on the adhesive layer 400. However, this synthetic leather configuration cannot meet the requirements for a variety of applications.

Shoes, which are one of major applications of polyurethane synthetic leather, 15 are required to have more excellent properties than those of clothes, house interior materials and car interior materials. In other words, shoes should have sufficient ability to maintain their inherent properties against severe external influences. For instance, the synthetic leather useful for shoes is required to have adhesive strength, chemical-resistance property, cushiony property, etc. maintainable even under high 20 temperature and humidity conditions; however, the synthetic leather having the configuration of FIG. 1 fails to satisfy these requirements.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a water-based polyurethane

composite to be used in preparation of a synthetic leather, having excellent properties corresponding to natural leather, without using solvents causing environmental pollution.

Another object of the present invention is to provide a water-based polyurethane synthetic leather of the novel configuration being able to maintain a high adhesive strength and chemical-resistance property and also exhibit a good cushiony property even under high temperature and humidity conditions.

The inventors of the present invention, after having carried out extensive research and many experiments, made a water-based polyurethane composite, having a viscosity within a specific range, by adding fine particles of a specific dimension to a polyurethane chain-extended product synthesized through a water-based polymerization reaction, and also found that a synthetic leather, particularly, a porous layer of the synthetic leather, made of the water-based polyurethane composite, has very similar properties, particularly, a cushiony property, to those of solvent-based polyurethane synthetic leather. Moreover, we found that in the case where, without adding a separate adhesive layer between a top skin layer and porous layer, a water-based polyurethane adhesive layer is added between a base layer and porous layer, the resulting synthetic leather can exhibit a high adhesive strength and chemical-resistance property as well as a good cushiony property even under high temperature and humidity. The present invention was accomplished on the basis of these findings.

According to the present invention, there is provided a water-based polyurethane composite which comprises (i) a water-based polyurethane chain-extended product and (ii) fine particles of the mean particle diameter of 0.5 ~ 50 μm ,

contained at 0.1 ~ 30% by weight based upon the total weight, and which has a viscosity of 500~100,000 cps.

This water-based polyurethane composite is particularly useful in preparing a porous layer of synthetic leather, and the synthetic leather thus prepared exhibits a 5 good cushiony property comparable to that of the synthetic leather made using a solvent-based polyurethane resin.

The term "water-based polyurethane chain-extended product" used in the present disclosure means a product which includes hydrophilic ionic groups in the polymer structure of polyurethane, synthesized in a water-based manner, so that it can 10 be stably dispersed in water. As such, the water-based polyurethane chain-extended product need not use an organic solvent, such as DMF, during the preparation procedure thereof, different from a solvent-based polyurethane chain-extended product. The type of this water-based polyurethane chain-extended product is not particularly limited, so long as it has the characteristics as described above.

15 As an example of the water-based polyurethane chain-extended product, it can be produced by reacting an isocyanate compound (a) having at least two isocyanate groups, an organic compound (b) having at least two isocyanate-reactive groups, and an organic compound (c) having one or two isocyanate-reactive groups and at least one hydrophilic ionic group to synthesize a polyurethane prepolymer (d) which has an 20 isocyanate group at both ends, respectively, and the hydrophilic ionic groups at 0.1 ~ 10 moles per molecule and also a number-average molecular weight of 1,000 ~ 30,000; and neutralizing, water-dispersing, and chain-extending the prepolymer (d) to obtain a dispersed water-based polyurethane chain-extended product. The parameters

such as the amount of each group and the molecular weight, as described above, represent the optimal condition for accomplishment of the present invention, unless a separate explanation therefor is provided hereinafter.

As the polyurethane prepolymer is neutralized and dispersed in water, a self-emulsified dispersant in which hydrophilic ionic groups are exposed at the surface thereof is formed to show a good dispersability to water. When a chain-extending compound ("chain extender") is added to a disperse solution prepared thus, functional groups of the chain extender react with the unreacted, residual isocyanate groups of the prepolymer to produce a water-based polyurethane chain-extended product.

The fine particles of organic and/or inorganic solid material, to be added to the water-based polyurethane chain-extended product, can be uniformly dispersed in the chain-extended product by stirring to give a desired polyurethane composite. During such dispersing procedure, the fine particles allow air, which is introduced into the composite and/or has been contained in the fine particles (including air present inside of the particles and/or on the surface of the particles), to be held within the composite such that the resulting synthetic leather, particularly, the porous layer thereof can exhibit a cushiony property. Further, the fine particles also serve as fillers helpful to maintain the structure of the porous layer.

The mean diameter of fine particles is preferably in the range of 0.5 ~ 50 μm as defined above. If the mean particle diameter is excessively small, it is difficult for the particles to uniformly disperse and also the ability to form air pockets decreases; on the other hand, if the mean diameter is excessively large, the particles tend to get together to the upper or lower portion of a synthetic leather due to the gravity thereof.

or make a synthetic leather stiff, which is not desirable. However, where fine particles added are present in an aggregated form, the particle size beyond the upper limit as described above is also acceptable to exhibit the effect intended by the present invention.

5 The addition amount of fine particles is preferably in the range of 0.1 ~ 30% by weight based upon the total weight of composite as defined above. If the addition amount is excessively small, it is difficult to have the ability to form air pockets and support the structure (e.g., a porous layer); on the other hand, if the addition amount is excessively large, it results in the increase of viscosity to decrease the moldability of
10 synthetic leather and make a synthetic leather stiff, which is not desirable. The addition amount is more preferably in the range of 1 ~ 10% by weight.

The viscosity of a water-based polyurethane composite according to the present invention is important in view of forming air pockets, layered structure-forming ability, and structure-supporting ability, and is determined by a variety of
15 factors such as the molecular weight of water-based polyurethane chain-extended product, the mean diameter and addition amount of fine particles, the amount of water used for dispersion, etc. Such viscosity is preferably in the range of 500 ~ 100,000 cps as defined above; if the viscosity is excessively low, the air-pocket forming and structure-supporting abilities decrease; on the other hand, if the viscosity is
20 excessively high, the layered structure-forming ability decreases. The viscosity of composite is more preferably in the range of 5,000 ~ 30,000 cps.

In an embodiment, other components may be further added such as thickener, cross-linking agent (or curing agent), antifoaming agent, pigment, dispersing agent,

forming agent, surfactant, leveling agent, wetting agent, water-and-oil repellent, and the like, within the range where the effect of the present invention is not damaged. The addition amount of these components is generally in the range of 0.05 ~ 10% by weight based upon the total weight of composite.

5 The water-based polyurethane composite according to the present invention is preferably useful in forming the porous layer of a synthetic leather.

An exemplary method for preparation of the porous layer is illustrated in below.

The preparation method comprises adding fine particles having a mean diameter of 0.5 ~ 50 μm to a water-based polyurethane chain-extended product at 0.1 ~ 30% by weight on the basis of the total weight of a composite, then stirring to produce a water-based polyurethane composite containing many fine bubbles and having a viscosity of 500 ~ 100,000 cps, and coating the composite on a base layer at a thickness of 0.1 ~ 3 mm to form a porous layer. In an embodiment, a top skin layer 10 may be further added on the porous layer. In another embodiment, an adhesive layer 15 may be further added between a top skin layer and porous layer, between a porous layer and based layer, or between a top skin layer and porous layer and simultaneously a porous layer and base layer so as to secure a further strong bonding.

The particularly preferable configuration of a water-based polyurethane synthetic leather comprises (i) a base layer being made of fabric itself or resin-impregnated fabric and forming the base of a synthetic leather, (ii) an adhesive layer being situated on the base layer and serving to strengthen the bonding of a porous layer and the base layer, (iii) a porous layer being situated on the adhesive layer and

providing a cushiony property of natural leather, and (iv) a top skin layer being situated on the porous layer and forming the top of a synthetic leather.

This configuration of a water-based polyurethane synthetic leather is characterized in that an adhesive layer is added between a base layer and a porous layer, and the resultant synthetic leather is very useful as a material for shoes. The adhesive layer serves to strengthen the adhesive strength between a base layer and porous layer to provide a high adhesive strength required for a leather material for shoes, particularly under a high temperature and humidity condition, thereby providing the properties of synthetic leather required to the so-called "jungle test".
5 This adhesive layer is not particularly limited so long as it satisfies the above requirements, and it can be made of materials used in the art to which the present invention pertains.
10

The top skin layer can be made of, for example, a polyurethane resin obtained by adding a curing agent to a water-based polyurethane chain-extended product as
15 described above to be subjected to cross-linking reaction.

The porous layer serves to provide a good cushiony property because it contains many fine bubbles and is preferably made of, but is not limited to a water-based polyurethane composite containing fine particles as described above.

As a fabric for the base layer, used can be synthetic or natural woven fabrics,
20 non-woven fabrics, knitted fabrics, microfiber fabrics, high density fabrics, etc. which are well known to those skilled in the art. Furthermore, the base layer can be in the form of fabric itself or resin-impregnated fabric. The resin-impregnated fabric is the fabric prepared, for example, by impregnating a fabric with a polyurethane resin, and

the kind of impregnation resins and methods for impregnation are known to those skilled in the art, thus the detailed description thereof is omitted in the present disclosure.

5 The method for preparation of a water-based polyurethane synthetic leather with the above configuration comprises, for example, the steps of:

- (A) coating a water-based polyurethane resin on a thin release film at a thickness of 0.05 ~ 1 mm to form a top skin layer, followed by drying;
- (B) coating a water-based polyurethane resin containing fine bubbles on the top skin layer at a thickness of 0.1 ~ 3 mm to form a porous layer, followed by 10 drying;
- (C) coating an adhesive resin on the porous layer at a thickness of 0.01 ~ 1 mm to form an adhesive layer; and
- (D) adhering a fabric itself or resin-impregnated fabric to the adhesive layer to form a base layer, followed by removing the release film.

15 The release film which is temporarily attached on the top skin layer is preferably embossed to give the appearance corresponding to the surface of a natural leather.

The steps of coating the top skin layer and porous layer may be performed by repeating the coating/drying procedure one or more times so that the final layer 20 thickness is in the above-defined range. The drying procedures in the steps (A) and (B) can be carried out at 70 ~ 150°C for 1 ~ 60 minutes. An excessively low drying temperature requires a long drying time to reduce the process efficiency, whereas an

excessively high drying temperature deteriorates the leather; for example, the layers are cracked or warped.

In the step (D), after coating of fabric or resin-impregnated fabric, a pressure may be applied thereto such that a stronger adhesion can be accomplished between the adhesive layer and base layer and simultaneously the surface of the top skin layer is formed corresponding to the embossed surface of the release film.

Also, in the step (D), after forming of the base layer and before removal of the release film, an aging step is further included. The aging can be performed at approximately 50 ~ 100°C for 1 ~ 24 hours but the aging temperature and time are not limited thereto.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be illustrated below in more detail. First, materials exemplified above in connection with a water-based polyurethane composite will be illustrated in more detail and some of the same are also involved in the preparation of a top skin layer and adhesive layer.

The isocyanate compound (a) is a compound having at least two isocyanate groups (-NCO) per molecule, and preferably two isocyanate groups per molecule. The isocyanate compound includes, for example, tetramethylene diisocyanate, hexamethylene diisocyanate, octamethylene diisocyanate, decamethylene diisocyanate, dodecamethylene diisocyanate, cyclohexane-1,3-diisocyanate, cyclohexane-1,4-diisocyanate, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane, bis-(4-isocyanatomethyl)cyclohexane, bis-(4-isocyanato-3-

methyl-cyclohexyl)-methane, etc, which are well known to those skilled in the art.

The term “isocyanate-reactive group” used in the present disclosure, which is a group able to react with an isocyanate group (-NCO) of the isocyanate compound (a), means a group having a reactive hydrogen(s), for example, hydroxyl group (-OH),
5 thio group (-SH), primary or secondary amine (-NH₂, $\text{--}^{\text{l}}\text{N}\text{--H}$), etc.

The organic compound (b) which has at least two isocyanate-reactive groups per molecule includes, for example, dihydroxy polyesters made by reaction of a dicarboxylic acid such as succinic acid, adipic acid, suberic acid, azelaic acid, phthalic acid, isophthalic acid, terephthalic acid, etc. with a diol compound such as ethylene
10 glycol, propylene glycol, diethylene glycol, butanediol, hexanediol, neopentene glycol, 2-methylpropanediol, etc.; dihydroxy polyacetones such as ϵ -caprolactone; dihydroxy polycarbonates made by reaction of an diarylcarbonate and a diol compound; various dihydroxy polyethers; dithio polythioethers; dihydroxy polyacetals, and the like, which are well known to those skilled in the art.

15 The organic compound (c) which has a hydrophilic ionic group in a side chain of molecule allows a polyurethane prepolymer to exhibit the water dispersability and has an isocyanate-reactive group able to react with the isocyanate compound (a) at one or both ends thereof. Accordingly, the organic compound (c) composes a component of polyurethane prepolymer backbone by reaction with the isocyanate compound (a),
20 and also is placed on the surface of a dispersant, when a synthesized prepolymer is dispersed in water, to allow the prepolymer to show dispersibility.

The hydrophilic ionic group can be an anionic or cationic group when

neutralized and includes, for example, $-CO_2-$, $-SO_3-$, $-\overset{|}{N}^+$, $-\overset{|}{S}^+$, etc. Among them, the carboxylic anionic group ($-CO_2-$) is particularly preferred. The organic compound (c) having the carboxylic group as an ionic group includes, for example, a dihydroxy carboxylic acid compound having hydroxyl groups at both ends and also at least one carboxylic group. As representative examples thereof, there are citric acid, tartaric acid, dimethylpropionic acid (DMPA), dimethylbutyric acid (DMBA), etc.

In an embodiment, in addition to the organic compound (c), another organic compound (c') having a hydrophilic non-ionic group in the backbone or side chain and isocyanate-reactive groups at both ends thereof may be further added at 1 ~ 50% by weight based upon the total weight of prepolymer, then subjected to polymerization reaction, to produce a water-based polyurethane prepolymer having better water dispersability. The prepolymer further including the organic compound (c') can maintain the stable water dispersability even under varying pH. This hydrophilic non-ionic group includes, for example, hydrophilic ethylene oxide unit ($-CH_2O-$).

The amount of isocyanate compound (a) and organic compound (b) is dependent upon the molecular weight of a synthetic polyurethane prepolymer (d) and whether isocyanate groups are present at one or both ends. This amount is also dependent upon the amount of hydrophilic ionic groups contained in one molecule of a synthesized polyurethane prepolymer. Therefore, the amount of these components need not to be particularly restricted, because the molecular weight of polyurethane prepolymer, the condition whether isocyanate groups are present at one or both ends, and the amount of hydrophilic ionic group contained in one molecule of a synthesized prepolymer can be naturally determined in the range already mentioned.

A method for preparation of a polyurethane prepolymer by reaction of an isocyanate group-containing compound and a isocyanate-reactive group-containing compound is already known to those skilled in the art, thus the detailed explanation is omitted in the present disclosure.

5 The polyurethane prepolymer thus prepared is neutralized, water-dispersed and chain-extended to produce a water-based polyurethane chain-extended product.

Generally, a hydrophilic ionic group is present as a potent ionic group in the organic compound (c) in which the potent ionic group shows a low solubility to water.

If this potent group is reacted with a neutralizer before or after the polymerization

10 reaction, it then converts to an anionic or cationic group of a high solubility as mentioned above. The kind of neutralizer is determined depending upon the characteristic of ionic group; for example, where the ionic group is anionic, a basic

compound is employed as a neutralizer, and where the ionic group is cationic, an acidic compound is employed. The basic neutralizer includes, for example, soluble

15 tertiary amines, alkali metal hydroxides, etc. and the acidic neutralizer includes, for example, organic or inorganic acids such as hydrochloric acid, sulfuric acid, nitric

acid, benzylchloride, epichlorohydrine, glycolic acid, dimethylsulfate, hydrobromic acid, trimchloroacetic acid, trifluoroacetic acid, sulfonic acids, acetic acids, and the like.

The neutralizer is preferably used at an amount of neutralizing all hydrophilic

20 ionic groups; however, in any case, only 50% thereof is also acceptable.

The amount of water used in dispersion is not particularly limited but can be properly determined in consideration of other factors.

When the polyurethane prepolymer (d) is neutralized and then dispersed in

water, among isocyanate groups present at the end of polymer, the isocyanate groups contacting water react with water to generate carbon dioxide (CO_2) and convert to amine groups (-NH₂), and the remaining isocyanate groups continue to be present in the state of an active form. These active isocyanate groups react with a chain extender
5 (e) added to a dispersion of polyurethane prepolymer (d) to produce a polymerized polyurethane chain-extended product (f).

Accordingly, the chain extender (e) must have at least two isocyanate-reactive groups per molecule. This chain extender (e) includes, for example, diamine compounds such as ethylene diamine, hexamethylene diamine, isophorone diamine,
10 etc.; diol compounds such as ethylene glycol, diethylene glycol, 1,4-butane diol, etc.; triol compounds such as glycerin; triamines such as melamine, diethylene triamine, etc.; triethylene tetramine, N-methyl-diethanolamine, N-butyl-diethanolamine, N-oleyldiethanolamine, N-cyclohexyl-diethanolamine, N,N-dimethylhydrazine, N,N-dimethylethylenediamine, N,N-dimethyl-propylenediamine, and the like.

15 Chain-extending reaction can be carried out by adding the prepolymer (d) into a reactor containing water and then adding the chain extender (e) thereto, or by adding the chain extender (e) into a reactor containing water and then adding the prepolymer (d) thereto. The former manner is more desirable in view of control of the molecular weight of a water-based polyurethane chain-extended product (f), a high reactivity,
20 etc.

One of the features of the present invention is in that a composite, made by adding fine particles having specific properties to the water-based polyurethane chain-extended product (f) synthesized above, is useful in preparation of a synthetic leather,

and moreover, this synthetic leather can provide excellent properties comparable to a solvent-based synthetic leather.

The fine particles which make it possible to prepare a water-based polyurethane synthetic leather having excellent properties are organic and/or inorganic materials and are preferably inorganic materials such as silica. The fine particle can be in the form of powder, bead, plate or fiber, or other certain forms. The bead-formed fine particle includes, for example, commercially available ZeospheresTM (ceramic hollow microspheres), ScotchliteTM Glass bubbles (3M Chemicals), and the like.

A fine particle of the porous structure is more desirable because the porous structure can hold a relatively large amount of gas (inert gas, air and the like depending upon reaction conditions) on preparation of a synthetic leather to be able to further increase a cushiony property. The type of porous structure is not particularly limited. In other words, the particle itself may have a porous surface structure or porous internal structure, and in any case, a plurality of fine particles may aggregate to form a porous aggregating structure. A commercially available fine particle having the porous internal structure includes, for example, Matsumoto MicrosphereTM MFL series (Matsumoto Yushi-Seiyaku Co., Ltd) which are hollow polymer microspheres having a particle diameter of 20 ~ 100 μm , K1 (3M Chemicals), etc. In an embodiment, the fine particle is a thermo-expandable microsphere or microporous aggregate. A commercially available, thermo-expandable microsphere includes, for example, EXPANCELTM (Akzo Nobel), Matsumoto MicrosphereTM F Series (Matsumoto Yushi-Seiyaku Co., Ltd), etc. which are microspheres having a particle diameter of 10 ~ 30 μm , respectively, and can expand to more than double their size when heated. Where the heated microspheres are contained in a composite according

to the present invention, some are in the expanded form and the others are in the broken form, which helps a resulting synthetic leather to exhibit a cushiony property. The microporous aggregate includes, for example, a commercially available NIGEL™, NIPSIL™ (Nippon Silica Industrial Co., Ltd.), etc. Where the microporous aggregates are contained in a composite according to the present invention, some polyurethane resin of the composite infiltrates into some pores of the aggregates to reinforce the bonding of the aggregates and composite, while the remaining pores into which the resin did not infiltrate can provide a good cushiony property.

A fabric used in the base layer of a synthetic leather may be various woven fabrics, non-woven fabrics, knitted fabrics, microfiber fabrics, high density fabrics, and the like, known to the art relevant to synthetic leathers, and also may be a fabric itself or a resin-impregnated fabric. The resin-impregnated fabric can be made, for example, by impregnating polyurethane resin into a fabric in the synthetic leather-manufacturing process. A water-based polyurethane composite is spread on the fabric to form a porous layer. As a resin used in the resin-impregnating fabric, polyurethane resins for a synthetic leather known to those skilled in the art can be employed. It is preferably a water-based polyurethane composite, not containing fine particles, according to the present invention, i.e., the water-based polyurethane chain-extended product (f). Desirably, as mentioned already, an adhesive layer is added between a base layer and porous layer so as to increase the adhesive strength between these layers. An adhesive agent for the adhesive layer is not particularly limited so long as it can increase the adhesive strength between these layers.

To the synthetic leather prepared thus, a top skin layer may be further added by top coating, if necessary; the top coating method and materials therefor are known

to those skilled in the art, thus their detailed explanation is omitted in the present disclosure.

If required, other steps can be further included in the synthetic leather preparation method according to the present invention within the range that the effect 5 of the present invention would not be damaged, which should be interpreted to be included to the scope of the present invention. For example, a trace of organic solvent such as acetone may be added to easily control the viscosity of the prepolymer (d). Also, an emulsifier may be further added to obtain a better dispersion of the prepolymer (d). Further, to the water-based polyurethane composite according to the 10 present invention may be further added a thickener for increasing the viscosity of composite, a cross-linking agent (or curing agent) for increasing the strength, a antifoaming agent for controlling the form of cells (pores), a pigment for coloring, and other forming agent, surfactant, leveling agent, wetting agent, water-and-oil repellent, etc. The thickener includes, for example, polyurethane-based compound, polyacrylic 15 ester-based compound, cellulose derivatives, etc. The cross-linking agent includes, for example, polyisocyanate-based compound, methylolmelamine-based compound, aziridine-based compound, oxazoline-based compound, etc. The antifoaming agent includes, for example, silicon-based compound, alcohol-based compound, fatty acid-based compound, etc. The pigment includes, for example, titanium dioxide, carbon 20 black, etc. However, these are only exemplary and other known ones can be included.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a schematic view of the cross-sectional configuration of a prior art water-based polyurethane synthetic leather;

FIG. 2 is a schematic view of the cross-sectional configuration of a water-based polyurethane synthetic leather according to the present invention;

FIG. 3 is a process for preparation of the water-based polyurethane synthetic leather of FIG. 2; and

5 FIG. 4 is a scanning electron microscope photograph of the cross section of the synthetic leather prepared in Example 6, and FIG. 5 is an enlargement thereof.

Designation of the reference numerals

100: water-based polyurethane synthetic leather

200: base layer

10 300: porous layer

400: adhesive layer

500: top skin layer

600: release film

DESCRIPTION OF THE PREFERRED EMBODIMENTS

15 The present invention will now be illustrated in more detail by the following preparations and examples. However, it will be understood that the present invention is not limited to these specific preparations and examples, but is susceptible to various modifications that will be recognized by the skilled person in the art to which the present invention pertains.

20 Preparation 1: Preparation of polyurethane prepolymer

120.8 g of isophrone diisocyanate as an isocyanate compound (a), 469 g of

polytetramethylglycol as an organic compound (b), and 42.2 g of dimethylpropionic acid as an organic compound (c) were reacted at 80°C for 3 hours to synthesize 632 g of polyurethane prepolymer.

Preparation 2: Preparation of water-based polyurethane composite

5 To the polyurethane prepolymer synthesized in Preparation 1, added was triethylamine as a basic neutralizer. 632 g of the polyurethane prepolymer thus neutralized was added to a reaction bath containing 1,000 L of water and stirred at 500 rpm to perform dispersion, and 13 g of ethylene diamine as a chain extender was added thereto to carry out an extension reaction for 2 hours to synthesize a
10 polyurethane chain-extended product. To the reaction solution, fine particles, thickener, antifoaming agent, pigment, curing agent, etc. as defined in Table 1 below were added and stirred at 500 rpm for 30 ~ 60 minutes to produce a water-based polyurethane composite (slurry). The produced polyurethane composite was measured to have a viscosity of approximately 5,000 ~ 30,000 cps depending upon the addition
15 amount of thickener.

Examples 1 ~ 5: Preparation of synthetic leather

The water-based polyurethane composite prepared in Preparation 2 was coated on a non-woven fabric for synthetic leather as a base layer at a thickness of 1 mm, and dried at 100°C for 5 minutes and then again 130°C for 30 minutes to produce
20 a synthetic leather semi-product in which a porous layer is formed directly on a base layer.

1 g of a thickener (TAFIGEL PUR-40; Munging Chemie Corp.) and 10 g of a

pigment dispersion (WHITE 100; K. F. Tech Corp.) were added to a water-based polyurethane resin (Genud-SLT-220; Gentrol) and sufficiently stirred, then the resultant mixture was coated on a release film of the A4 size at a thickness of 0.1 mm and dried at 130°C for 2 minutes, followed by re-coating of the same mixture at the 5 total thickness of 0.15 mm and then drying at 130°C for 2 minutes, to form a top skin layer on the release film. On the top skin layer, coated was a water-based polyurethane resin (Genud-SLT-220; Gentrol) as an adhesive agent at the total thickness of 0.3 mm to form an adhesive layer, shortly thereafter the intermediate product comprising the base layer and porous layer, as prepared above, was applied thereto so that the porous 10 layer of the intermediate product faces the adhesive layer. After pressing, the release film was removed to produce a synthetic leather. The properties of the produced synthetic leather were tested according to the below methods and the results thereof are described in Table 1.

[Property Test 1]

- 15 - Cushiony property test: when a specimen was pressed by hand, its softness and restorability were evaluated. The supreme quality was set to 100%, and the relative value was estimated on the basis of that supreme quality. Where the value is less than 30%, the material fails to exhibit a cushiony property as a synthetic leather.
- 20 - Abrasion test: a specimen was subjected to the abrasion test according to ASTM D3884 to express the abrasion amount with mg.
- Room temperature bending test ("Bally Flex test"): a specimen was hung over a bending tester to be subjected to the repeated bending test at 25°C. The

bending number was counted until the specimen cracked.

- Hydrolysis resistance test: a specimen was dipped in aqueous 10% NaOH, and after the lapse of a certain time, cracking of the surface was measured.

[Table 1]

| Example | | 1 | 2 | | 3 | 4 | | 5 |
|---------------------|--------------------------|----------|----------|----|----------|----------|----|----------|
| Fine particles | Kind | AZ-360 | AZ-360 | K1 | AZ-360 | AZ-360 | K1 | AZ-360 |
| | Amount (g) | 4 | 3 | 2 | 4 | 2 | 1 | 4 |
| Thickener | Kind | TAFIGEL | TAFIGEL | | TAFIGEL | TAFIGEL | | TAFIGEL |
| | Amount (g) | 0.5 | 0.5 | | 0.5 | 0.5 | | 0.5 |
| Antifoaming agent | Kind | SN | SN | | SN | SN | | SN |
| | Amount (g) | 0.1 | 0.1 | | 0.1 | 0.1 | | 0.1 |
| Pigment | Kind | KP-White | KP-White | | KP-White | KP-White | | KP-White |
| | Amount (g) | 5 | 5 | | 5 | 5 | | 5 |
| Cross-linking agent | Kind | WS-500 | WS-500 | | WS-500 | WS-500 | | WS-500 |
| | Amount (g) | - | 3 | | 2 | 3 | | 4.5 |
| Property | Cushiony property (%) | 95 | 70 | | 80 | 60 | | 50 |
| | Abrasion (mg) | 10 ~ 20 | 10 ~ 20 | | 10 ~ 20 | 10 ~ 20 | | 10 ~ 20 |
| | Light resistance (Grade) | 5 | 5 | | 5 | 5 | | 5 |
| | Bally Flex (Number) | 80,000 | 56,000 | | 40,000 | 50,000 | | 48,000 |
| | Hydrolysis resistance | Good | Good | | Good | Good | | Good |

5 * AZ-360(NIGEL AZ-360) : Nippon Silica Co., Ltd.

- * K1 : 3M Corp.
 - * TAFIGEL(TAFIGEL PUR-40) : Munging Chemie Corp.
 - * SN(SN Defoamer-313) : San Nopco Korea Ltd.
 - * KP-White : K. F. Tech Corp.
- 5 * WS-500(EPOCROS WS-500) : Nippon Shokubai Co., Ltd.

As seen in Table above, all synthetic leathers prepared in Examples 1 ~ 5 according to the present invention exhibited an excellent cushiony property and other properties required of synthetic leather.

Comparative Example 1

10 A synthetic leather was prepared in the same manner as in Examples 1 ~ 5 except for not adding fine particles, and was subjected to the property tests. The result showed that general properties such as abrasion resistance, light resistance, etc. are not bad, but the cushiony property was estimated to be 20% which fails to attain the level required of synthetic leather.

15 Example 6: Preparation of synthetic leather

1 g of a thickener (TAFIGEL PUR-40; Munging Chemie Corp.) and 10 g of a pigment dispersion (WHITE 100; K. F. Tech Corp.) were added to a water-based polyurethane resin (Genud-SLT-220; Gentrol) and sufficiently stirred, then, as illustrated in Fig. 3, the resultant mixture was coated on a release film 600 of the A4 size at a thickness of 0.1 mm and dried at 130°C for 2 minutes, followed by re-coating of the same mixture at the total thickness of 0.15 mm and then drying at 130°C for 2 minutes, to form a top skin layer 500 on the release film 600. The water-based

polyurethane composite, as prepared in Preparation 2, was coated on the top skin layer 500 at the total thickness of 0.3 mm and dried at 100°C for 5 minutes, then the same composite was again coated thereon at the total thickness of 0.6 mm and dried at 100°C for 5 minutes to form a porous layer 300. On the porous layer 300, coated was
5 the same resin as that used to the top skin layer at the total thickness of 0.8 mm to form an adhesive layer 400, shortly thereafter a non-woven fabric for a base layer 200 was applied to the adhesive layer 400 and dried at 100°C for 5 minutes to produce a layered-composite structure, which was then aged at 80°C for 12 hours. After the release film was removed, a water-based polyurethane synthetic leather 100 was
10 provided having the configuration of FIG. 2.

The synthetic leather was subjected to the property tests as described in Examples 1 ~ 5 and also an adhesion test below. The results thereof are described in Table 2 below.

[Property Test 2]

- 15 - Adhesion test: a rubber was adhered to a specimen, with the top skin layer of specimen facing the rubber, which was then hung over UTM equipment (LR-5K; Lloyd Co., Ltd.) to measure the force applied to the specimen until the separation thereof occurred.

The cross section of the synthetic leather produced above was observed
20 through a scanning electron microscope (SEM). A SEM photograph and an enlarged photograph thereof are shown in FIGS. 4 and 5, respectively. Referring to these photographs, it is ascertained that many fine particles and water drop-like cells are contained in a porous layer. The fine particles serve to support the porous layer so that

the porous cells can be held in the porous layer during preparation of the porous layer. Over the porous layer, shown is a top skin layer which has no fine particles and porous cells and contributes to the surface texture, strength, and other general properties of synthetic leather. It can also be shown that some of an adhesive layer below the 5 porous layer is infiltrated into a base layer. A high adhesive strength can be obtained from this configuration because the porous layer and adhesive layer are made of the same polyurethane-based resin to have affinity for ensuring good adhesion between the porous layer and adhesive layer, and also because some of the adhesive agent infiltrates into the base layer to result in an excellent adhesion between the adhesive 10 layer and base layer. As a result, a water-based polyurethane synthetic leather of this novel configuration can exhibit more excellent adhesive strength even under a high temperature and humidity condition, compared to the prior art water-based polyurethane synthetic leathers.

Comparative Example 2

15 The same water-based polyurethane composite as in Example 6 was coated on the same non-woven fabric as in Example 6 at a thickness of 0.1 mm and dried at 100°C for 5 minutes, and the same water-based polyurethane composite was again coated thereon at the total thickness of 0.6 mm and dried at 100°C for 5 minutes and then 130°C for 30 minutes to produce a synthetic leather semi-product, as shown in 20 FIG. 1, in which a porous layer 300 is formed directly on a base layer 200. Meanwhile, 1 g of a thickener (TAFIGEL PUR-40; Munging Chemie Corp.) and 10 g of a pigment dispersion (WHITE 100; K. F. Tech Corp.) were added to a water-based polyurethane resin (Genud-SLT-220; Gentrol) and sufficiently stirred, then the resultant mixture

was coated on a release film 600 of the A4 size at a thickness of 0.1 mm and dried at 130°C for 2 minutes, followed by re-coating of the same mixture at the total thickness of 0.15 mm and then drying at 130°C for 2 minutes, to form a top skin layer 500 on the release film 600. On the top skin layer 500, coated was a water-based polyurethane resin (Genud-SLT-220; Gentrol) as an adhesive agent at the total thickness of 0.3 mm to form an adhesive layer 400, shortly thereafter the intermediate product comprising the base layer 200 and porous layer 300, as prepared above, was applied thereto with the porous layer 300 of intermediate product facing the adhesive layer 400. After pressing, the release film was removed to produce a synthetic leather of FIG. 1. The produced synthetic leather was subjected to the property tests in the same manner as in Example 6 and the results thereof are described in Table 2 below.

[Table 2]

| | | Example 6 | Comparative Example 2 |
|-------------------|-----------------------|-------------------|-----------------------|
| Fine particles | Kind | NIGEL AZ-360 | NIGEL AZ-360 |
| | Amount (g) | 3 | 3 |
| Thickener | Kind | TAFIGEL PUR-40 | TAFIGEL PUR-40 |
| | Amount (g) | 0.5 | 0.5 |
| Antifoaming agent | Kind | SN Defoamer-313 | SN Defoamer-313 |
| | Amount (g) | 0.1 | 0.1 |
| Pigment | Kind | KP-White | KP-White |
| | Amount (g) | 5 | 5 |
| Curing agent | Kind | EPOCROS WS-500 | EPOCROS WS-500 |
| | Amount (g) | 1 | 1 |
| Property | Cushiony property (%) | 95 | 80 |

| | | | |
|--|--|-----------|-----------|
| | Adhesive strength (kg/cm ²) | 3.0 ~ 4.0 | 2.0 ~ 2.5 |
| | Abrasion resistance (mg) | 10 ~ 20 | 10 ~ 20 |
| | Light resistance (Grade) | 5 | 5 |
| | Bally Flex (Numbers) | 100,000 | 40,000 |
| | Hydrolysis resistance | Good | Good |

* NIGEL AZ-360 : Nippon Silica Co., Ltd.

* TAFIGEL PUR-40 : Munging Chemie Corp.

* SN Defoamer-313 : San Nopco Korea Ltd.

* KP-White : K. F. Tech Corp.

5 * EPOCROS WS-500 : Nippon Shokubai Co., Ltd.

As shown in Table 2, the synthetic leather prepared in Example 6 according to a preferable embodiment of the present invention has a good cushiony property and excellent adhesive strength of more than 3.0 kg/cm² which satisfies the minimal adhesive strength, 2.5 kg/cm², required of a synthetic leather for shoes. Moreover, 10 when a threshold force was applied, a base layer (e.g., resin-impregnated non-woven fabric) was separated, which shows that the adhesion between a porous layer and based layer is very good. On the other hand, the synthetic leather prepared in Comparative Example 2 shows a good cushiony property owing to the contained fine particles like in Example 6, but it has a low adhesive strength of 2.0 ~ 2.5 kg/cm² and 15 when a threshold force was applied, a porous layer and base layer were separated from each other, indicating an insufficient adhesion therebetween.

INDUSTRIAL APPLICABILITY

As described above, the water-based polyurethane composite according to the present invention can be prepared without organic solvents such as DMF causing environmental pollution. Furthermore, a synthetic leather which is made using the composite has good properties almost comparable to those of solvent-based polyurethane synthetic leather, in particular, an excellent cushiony property. In addition, the synthetic leather of a novel configuration according to the present invention exhibits a high adhesive strength and chemical resistance as well as a good cushiony property even under high temperature and humidity conditions.

Other embodiments and uses of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered exemplary only, with the scope of particular embodiments of the invention indicated by the following claims.

WHAT IS CLAIMED IS:

1. A water-based polyurethane composite comprising (i) a water-based polyurethane chain-extended product and (ii) fine particles of the mean particle diameter of 0.5 ~ 50 µm, contained at 0.1 ~ 30% by weight based upon the total weight of the composite, and having a viscosity of 500~100,000 cps.
5
2. The composite according to claim 1, wherein the water-based polyurethane chain-extended product is produced by reacting an isocyanate compound (a) having at least two isocyanate groups, an organic compound (b) having at least two isocyanate-reactive groups, and an organic compound (c) having one or two isocyanate-reactive
10 groups and at least one hydrophilic ionic group to synthesize a polyurethane prepolymer (d) which has an isocyanate group at both ends, respectively, and the hydrophilic ionic groups at 0.1 ~ 10 moles per molecule and also a number-average molecular weight of 1,000 ~ 30,000; and neutralizing, water-dispersing, and chain-extending the prepolymer (d) to obtain the water-based polyurethane chain-extended
15 product in the disperse form.
3. The composite according to claim 1, wherein the fine particle is of organic and/or inorganic material.
4. The composite according to claim 1, wherein the fine particle has a porous surface structure or porous internal structure, or a plurality of the fine particles
20 aggregate to form a porous aggregating structure.
5. The composite according to claim 1, wherein the composite further contains

one or more selected from the group consisting of thickener, cross-linking agent (or curing agent), antifoaming agent, pigment, dispersing agent, forming agent, surfactant, leveling agent, wetting agent, water-and-oil repellent, and the like, in the range of 0.05 ~ 10% by weight based upon the total weight of composite.

5 6. A method of using the water-based polyurethane composite according to one of claims 1 to 5 in preparation of the porous layer of a synthetic leather.

7. A water-based polyurethane synthetic leather of the configuration comprising
10 (i) a base layer being made of fabric itself or resin-impregnated fabric and forming the base of a synthetic leather, (ii) an adhesive layer being situated on the base layer and serving to strengthen the bonding of a porous layer and the base layer, (iii) a porous layer being situated on the adhesive layer and providing a cushiony property of natural leather, and (iv) a top skin layer being situated on the porous layer and forming the top of a synthetic leather.

8. The synthetic leather according to claim 7, wherein the porous layer is made
15 of a water-based polyurethane composite comprising (i) a water-based polyurethane chain-extended product and (ii) fine particles of the mean particle diameter of 0.5 ~ 50 μm , contained at 0.1 ~ 30% by weight based upon the total weight of the composite, and having a viscosity of 500~100,000 cps,

20 in which the water-based polyurethane chain-extended product is prepared by reacting an isocyanate compound (a) having at least two isocyanate groups, an organic compound (b) having at least two isocyanate-reactive groups, and an organic compound (c) having one or two isocyanate-reactive groups and at least one

hydrophilic ionic group to synthesize a polyurethane prepolymer (d) which has an isocyanate group at both ends, respectively, and the hydrophilic ionic groups at 0.1 ~ 10 moles per molecule and also a number-average molecular weight of 1,000 ~ 30,000; and neutralizing, water-dispersing, and chain-extending the prepolymer (d) to

5 obtain a water-based polyurethane chain-extended product in the disperse form.

9. A method for preparation of a water-based polyurethane synthetic leather, comprising steps of:

(A) coating a water-based polyurethane resin on a thin release film at a thickness of 0.05 ~ 1 mm to form a top skin layer, followed by drying;

10 (B) coating a water-based polyurethane resin containing fine bubbles on the top skin layer at a thickness of 0.1 ~ 3 mm to form a porous layer, followed by drying;

(C) coating an adhesive resin on the porous layer at a thickness of 0.01 ~ 1 mm to form an adhesive layer; and

15 (D) adhering a fabric itself or resin-impregnated fabric to the adhesive layer to form a base layer, followed by removing the release film.

Fig. 1

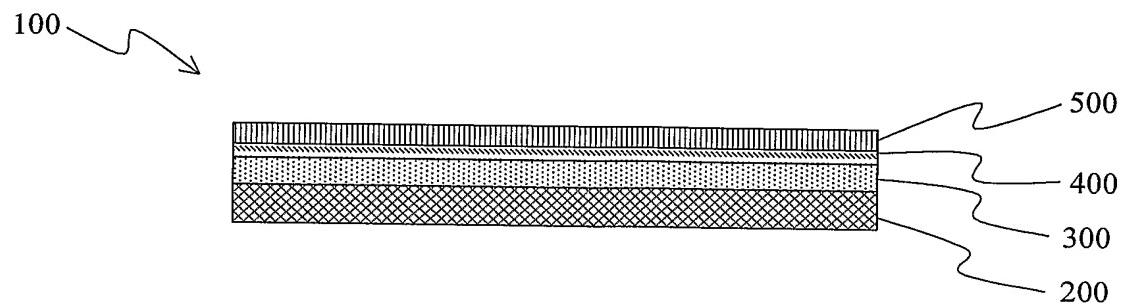


Fig. 2

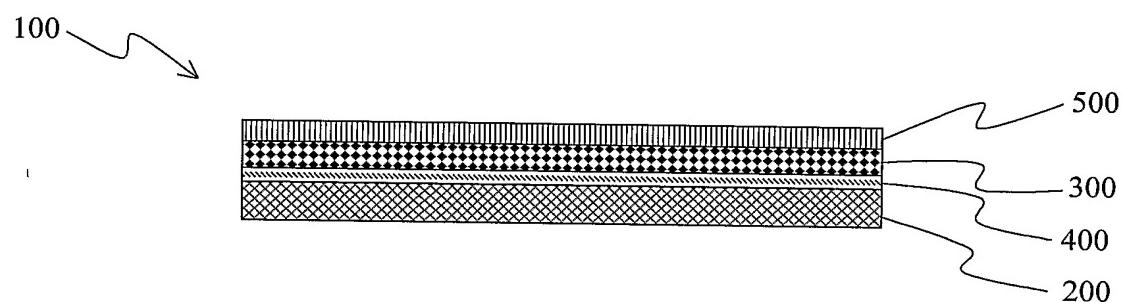


Fig. 3

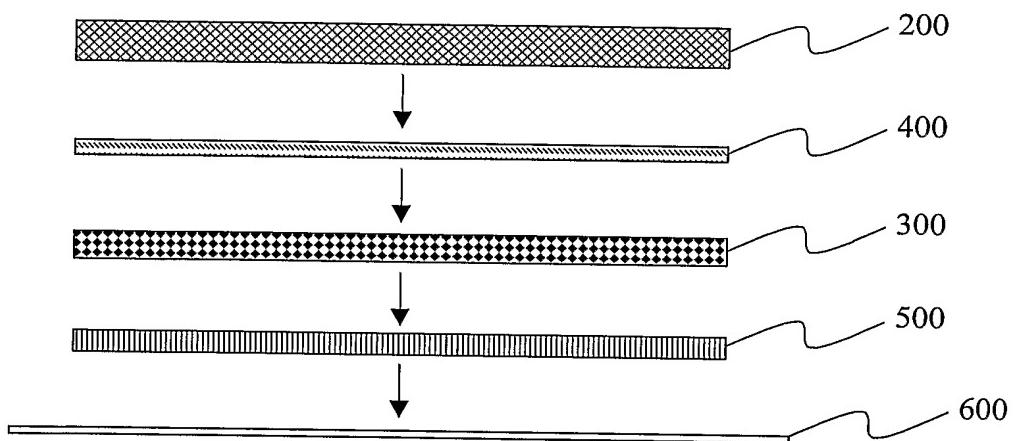


Fig. 4

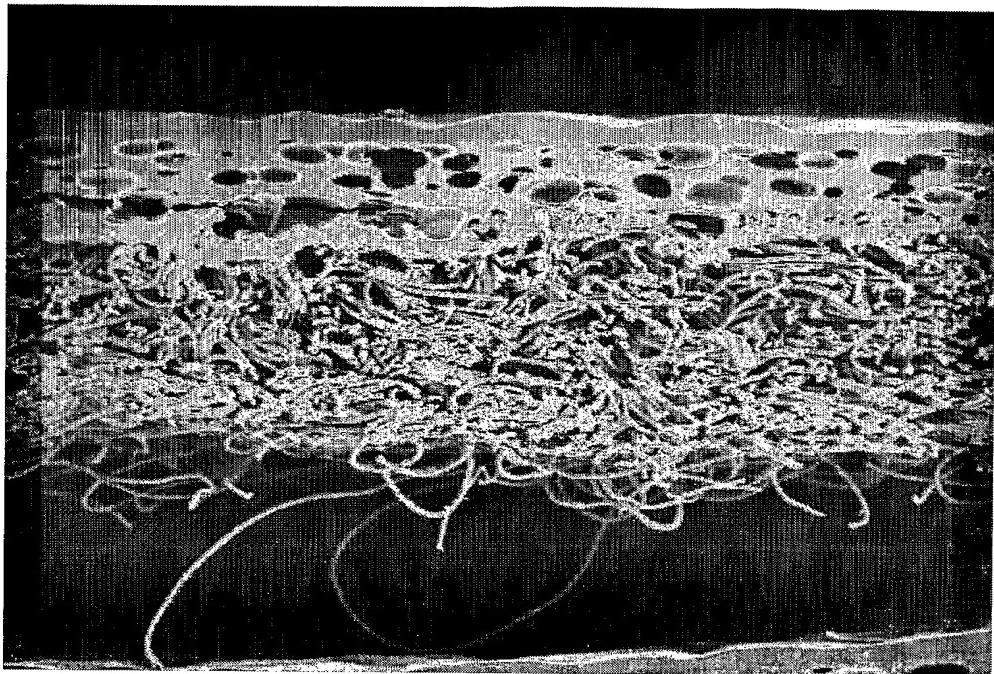
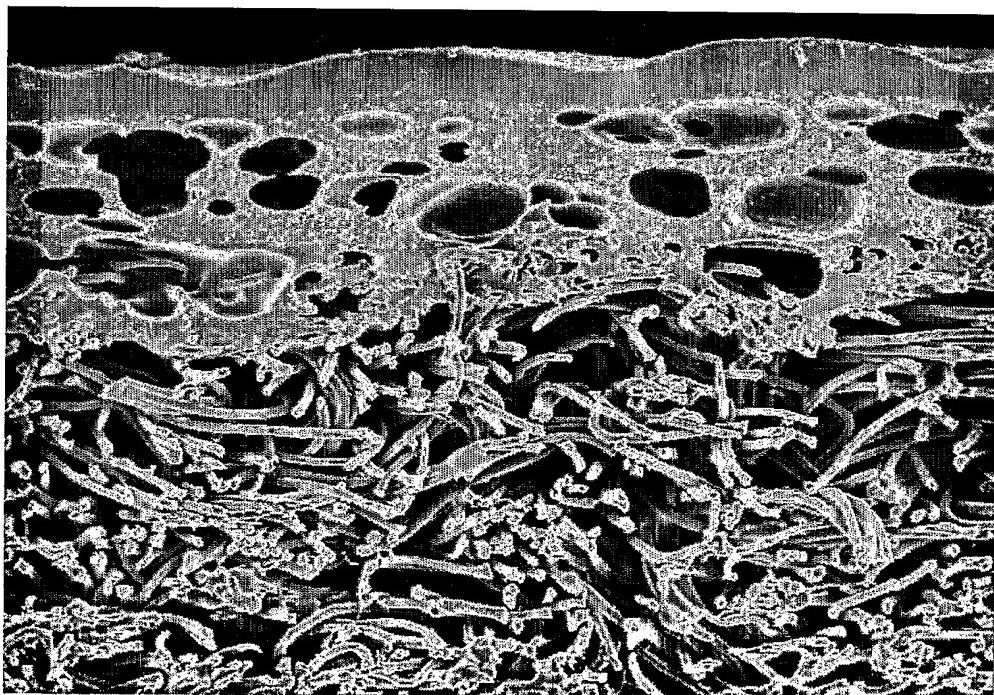


Fig. 5



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2004/000879

A. CLASSIFICATION OF SUBJECT MATTER**IPC7 C08G 18/00, D06N 3/14**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G, D06N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Patents and applications for inventions since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PAJ, eKIPASS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| Y | JP 2000-144580 A (KURARAY CO LTD) 26 MAY 2000 see example 1, paragraph 20 | 1 - 9 |
| Y | JP 2000-297211 A (DAINIPPON INK & CHEM INC) 24 OCT 2000 see paragraph 65, 66 | 1 - 9 |
| A | US 3993608 A (MINNESOTA MINING AND MANUFACTURING CO) 23 NOV 1976 see abstract, claim 1 | 1 - 9 |
| A | JP 2002-3780 A (NISSHIN STEEL CO.LTD) 9 JAN 2002 see the whole document | 1 - 9 |
| A | JP 62-162461 A (SUMITOMO METAL MINING CO.LTD) 18 JUL 1987 see the whole document | 1 - 9 |

Further documents are listed in the continuation of Box C.

See patent family annex.

- * Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search
16 JULY 2004 (16.07.2004)

Date of mailing of the international search report
16 JULY 2004 (16.07.2004)

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
920 Dunsan-dong, Seo-gu, Daejeon 302-701,
Republic of Korea
Facsimile No. 82-42-472-7140

Authorized officer
LEE, Dong Wook
Telephone No. 82-42-481-8115



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2004/000879

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|--|------------------|---------------------------------|------------------------------|
| JP 2000-144580 A | 26. 05. 2000 | NONE | |
| JP 2000-297211 A | 24. 10. 2000 | WO 00/46301 A1 EP 1164169 A1 | 10. 08. 2000 19. 12. 2001 |
| US 3993608 A | 23. 11. 1976 | NONE | |
| JP 2002-3780 A | 09. 01. 2002 | NONE | |
| JP 62-162461 A | 18. 07. 1987 | JP 7012590 B4 | 15. 02. 1995 |
| ----- END OF LINE ----- | | | |